Innovations

Real-Time Analysis of Incinerator Emissions: The Missing Link

Incineration has long been, and continues to be, one of the most cost-effective technologies for disposing of the world's growing volume of municipal and hazardous waste. Yet anyone who has been involved in an attempt to site an incinerator in recent years knows the political nightmare this process has become. The public has become extremely suspicious of the health and environmental impact of incinerators, and not without reason. Incinerators have been known to release unacceptably high levels of toxic substances into the air, including dioxins, furans, and other pollutants. Worse, there are no monitoring devices that can continuously measure trace gases in incinerator emissions to allow operators to know exactly what substances are being released and allow for quick corrective action.

To address the problems, several teams of university scientists are developing techniques for real-time emissions monitoring that may simultaneously allow industry to operate incinerators in the most efficient manner and assure the public that their health is being protected.

Incineration of hazardous wastes occurs in a number of contexts, including the Superfund program. Administered by the EPA, Superfund is charged with cleaning up hazardous wastes sites around the country. Hazardous waste from these sites is disposed of in various fashions, including incineration. Superfund administrators want to make sure that these and other incinerators are operated in a manner that doesn't endanger the public health and thus have provided funding for basic research in this field.

Under the Superfund Amendments and Reauthorization Act (SARA) of 1986, the federal government established a university-based grants program of basic research within the NIEHS to complement existing activities within the EPA and the Agency for Toxic Substances and Disease Registry. The SARA legislation mandates that the basic research program administered by NIEHS include:

- Methods and technologies to detect hazardous substances in the environment,
- Advanced techniques for the detection, assessment, and evaluation of the effects on human health of hazardous substances,
- Methods to assess the risks to human health presented by hazardous substances, and
- Basic biological, chemical, and physical methods to reduce the amount and toxicity of hazardous substances.

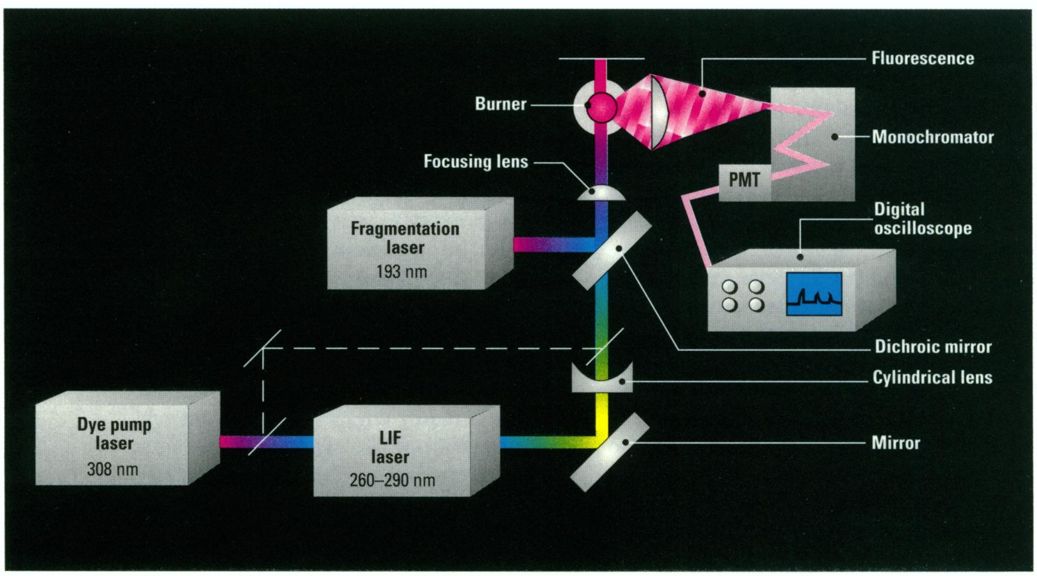
Currently, NIEHS's Superfund Basic Research Program funds 18 grants at 29 universities and institutions. Included in these are studies pertaining to combustion engineering, including the development of real-time monitors to determine the level of emissions in the combustion/pyrolysis process and basic methods to increase the efficiency of combustion and pyrolysis. Why is NIEHS involved in engineering-oriented research?

"First and foremost, our concern is public health," says William Suk, chief of the Chemical Exposures and Molecular Biology Branch at the NIEHS. "However, when you're dealing with issues of combustion engineering, you can't separate health and engineering. If you ask an engineer how to design an efficient incinerator, he or she will give you one answer. If you ask a health scientist, he or she will give you another. By bringing the two disciplines together, we hope to come up with the best answers for all concerned."

A Slow Burn

There are about 120 incinerators licensed to burn hazardous waste in the United States. Many of these are located in urban areas, where emissions could pose a health hazard to large numbers of people. The only established method for measuring trace gases in incinerator emissions is gas chromatography–mass spectrometry analysis of samples extracted from the stack and analyzed in a laboratory. This process may take hours or weeks to produce results, during which time significant amounts of toxic gases may be released into the atmosphere.

In the absence of continuous emissions monitoring technology, EPA requires all incinerators to undertake a trial burn—a series of tests intended to delimit the conditions and waste characteristics under which the applicable performance and emissions standards can be met. During the trial burn, emissions are sampled under various easily measured operating conditions such as furnace temperature and oxygen concentration. Parameters are established for these control variables under which tested emissions fall within EPA's standards. These parameters are then incorporated as operating requirements into the permit. Incineration under the conditions of the permit is subsequently assumed to meet all performance and emissions standards, generally for the life of the permit and without subsequent



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ELFFin magic. Excimer laser fragmentation fluorescence photodissociates chlorinated hydrocarbons into smaller carbon-chloride fragments and measures them by laser-induced fluorescence.

direct verification. However, there may be numerous circumstances for which such an assumption may be wrong for any given incinerator.

"Emissions [of toxic wastes] can reasonably be expected to increase significantly not only during start-ups, shutdowns, or upsets in combustion conditions, but also during periods of less-than-optimal performance resulting from lack of maintenance, or simply as a result of facility aging," states Richard Denison, senior scientist with the Environmental Defense Fund. "Yet data on aging effects or frequency of upsets are nonexistent, and such factors are rarely if ever incorporated into emissions estimates."

In addition to being unsatisfactory to the public and to regulators, this indirect method of emissions monitoring is a burden on industry as well.

"From an industry perspective, the permit requirements are overly prescriptive," says Randy Seeker, senior vice president of Energy and Environment Research Group based in Irvine, California. "You get fined if you operate outside the envelope, even though emissions may not be out of line. Development of continuous emissions monitoring systems is absolutely essential to the future of incineration," Seeker adds. "It's the missing link in the field of waste combustion."

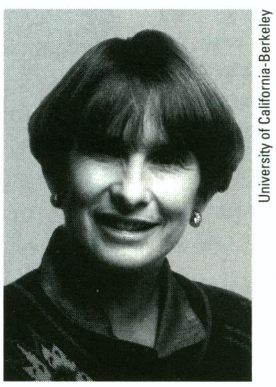
A Promising Technology

With funding from the NIEHS, research in the development of real-time monitoring of incinerator emissions has been taking place at the University of California at Berkeley and at the Massachusetts Institute of Technology. The work at U.C.-Berkeley is being done by a team that includes Charles McEnally, Robert Sawyer, Donald Lucas of Lawrence Berkeley Laboratory, and Catherine Koshland, the principal investigator.

Over the past five years, Koshland's team has been developing a measurement technique using excimer laser fragmentation fluorescence (ELFF) for the continuous monitoring of chlorinated hydrocarbons (CHCs). CHCs are an important waste category: almost 40% of incinerated waste contains some chlorine, and highly toxic CHCs are often found in incinerator emissions.

In brief, ELFF photodissociates CHCs into smaller carbon-chloride fragments and measures them by means of laser-induced fluorescence. The system is highly sensitive (able to measure CHC concentrations as low as 10 ppb), responds quickly (a few seconds or less), and can be used on site. The primary advantage of ELFF relative to other techniques is that it responds to all CHCs simultaneously and consequently does not rely on assumptions about which species are most likely to be emitted.

Koshland's experimental procedures with ELFF have involved pumping CHC-containing mixtures through a photolysis cell or out of a section of tubing into ambient air where they interact with laser beams. Two lasers are required: a fragmentation laser to photolyze the CHCs and a probe laser to excite the product carbon-chloride molecules.


University of California-Berkeley

Catherine Koshland

A dichroic mirror reflects the fragmentation beam into the measurement region; the probe beam passes through the rear edge of this mirror so that both beams follow the same path through the measurement region. The probe beam has a circular cross-section several millimeters in diameter that completely overlaps the fragmentation beam. A function generator-pulse generator combination triggers the lasers with an adjustable time interval between them. A photodiode in the vicinity of the lens and mirror detects reflection from both lasers. Its output provides a synchronization signal for the detection system and gives a measure of the time interval that is accurate to within the reproducibility.

A 20-mm diameter, 75-mm focal-length lens collects fluorescence emitted at a 90° angle to the beam paths. The intersection of the fragmentation beam with the solid angle viewed by the detection lens defines the actual measurement volume. A second lens directs the fluorescence through the entrance slit of a 0.3-m scanning monochromator coupled to a photomultiplier tube, whose output is digitized and recorded by a digital oscilloscope. Experiments with a mercury lamp show that the wavelength of the monochromator is accurate to within 0.2 nm. Koshland's team averages the emissions from 50 successive laser shots to remove changes in the signal caused by variations in the energy output of the lasers and aliasing from the digitization process.

For spatially resolved, on-site measurements with a detection time of 5 seconds, Koshland's team has achieved a detection limit for ethyl chloride of 100 parts per billion (ppb). The only interference found in flames was due to carbon-chloride fragments produced by chemical reactions; however, its concentration is negligible except at the front of the flame. Interferences from flame emissions were negligible, and no interfering fluorescence from other species was detected. The team has successfully used ELFF to detect other CHCs including chloromethane, several chloroethylenes and chloroethanes, and chlorobenzene. The detection limits for all compounds were 10 ppb or better for a 5-second response time. Based on these results, Koshland states the detection limit achieved by ELFF appears to meet EPA's requirements for incinerator emissions.

"The detection limits for emissions monitoring are not well defined since they depend upon assessment of health risks posed by specific incinerators," Koshland says. "However, some risk assessments have concluded that the risks from organic emissions allowed by current regulations are acceptable. These regulations require that toxic compounds present in the waste at concentrations of 100 to 10,000 ppm [parts per million] be destroyed by at least 99.99%. Thus, if we assume a dilution factor from waste to exhaust of 10, the maximum emission currently allowed is 100 ppb. Since that is for an individual waste compound, the total concentration of CHCs emitted may be somewhat higher. Therefore, the detection limit achieved by our current apparatus appears to be adequate for continuous monitoring."

Koshland emphasizes that an optimally designed ELFF using state-of-the-art lasers should be able to achieve significantly better results.

Measuring Metal Emissions

With their success in measuring CHC emissions, Koshland's team has recently expanded its research with ELFF to the detection of metal species. Metals are generated through a variety of industrial and combustion processes, such as metal plating, coal combustion, and waste incineration. Volatile toxic metal species including lead, nickel, chromium, and manganese are commonly found in coal, municipal waste, and hazardous waste streams at levels near 100 ppm. These and other toxic metal species can be transformed in the high-temperature region of a combustor through volatization, reaction, and nucleation, leading to a partitioning of metal between exit pathways. Public health officials are most concerned with the portion of the metal that exits through the stack, unabated by air-pollution control equipment. Research indicates that a significant portion of the atmospheric metals burden is generated by combustion sources; Koshland feels that this may pose the greatest risk from incinerators to public health.

In experiments with metals, Koshland's

group has used the same apparatus as used in their earlier work with CHCs, with the exception that only one laser was used instead of two. The metals experiments were conducted in the post-flame region of a Meeker burner issuing into ambient air. An aerosol of aqueous metal chloride salts was injected with the premixed stream into a premixed flat flame of methane and air stabilized on the burner.

In their experiments with ELFF, the team found that nickel, chromium, manganese, and lead stand out well against the background signal produced by fluorescence from species such as methyl groups and carbon, which are formed in excited states from fragmentation of products of incomplete hydrocarbon combustion. Averaged over 100 shots from the excimer laser, ELFF revealed detection limits of 3 ppb for nickel, 8 ppb for cromium, 4 ppb for maganese, and 0.5 ppb for lead.

Based on these results, Koshland's team believes ELFF can be a useful tool for measuring concentrations of many metal species in post-flame gases and is capable of meeting EPA's proposed regulations for metal emissions combusting devices. Continuing research will focus on development and extension of ELFF to other metal species.

Suggested Reading

- Dempsey CR, Oppelt ET. Incineration of hazardous waste: a critical review update. Air Waste Manage Assoc 43:25–73(1993).
- Kowalczyk GS, Choquette CE, Gordon GE. Chemical element balances and identification of air pollution sources in Washington, D.C. Atmos Environ 12:1143–1154 (1978).
- McEnally CS, Sawyer RF, Koshland CP, Lucas D. Sensitive in situ detection of chlorinated hydrocarbons in gas mixtures. Appl Optics 33:3977–3384 (1994).

Demonstration Phase

With the success of laboratory testing, Koshland's team is now conducting a commercial demonstration of ELFF. The demonstration is being conducted under a Cooperative Research and Development Authority agreement between the U.S. Department of Energy, U.C.-Berkeley, and Thermatrix, a chemical manufacturer based in San Jose, Calfornia. Thermatrix has a packed-bed thermal reactor which they use to destroy CHCs and PCBs. "We're using our laser technique to help Thermatrix explore how they can improve the operation of their system," says team member Don Lucas. "In addition to looking at CHCs, we will also determine whether ELFF can be used to detect PCBs." Testing is now underway at Lawrence Berkeley Laboratories, and should be complete in February 1995.

For Koshland's team and the other teams here and abroad working on continuous emissions monitoring, the stakes for developing a commercially viable system are high in terms of pride and recognition, if not in financial rewards.

"We've been working on this technique for five years and we look forward to perfecting it to the point where it reaches commercial application, " says Koshland. "A dependable continuous emissions monitoring system could go a long way toward improving the safety of incineration and other processes."

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Molecular Mechanisms of Metal Toxicity and Carcinogenicity

Volume 102, Supplement 3, presents the proceedings of the Second International Meeting on Molecular Mechanisms of Metal Toxicity and Carcinogenicity, held January 10–17, 1993, in Madonna di Campiglio, Italy. The main objective of the meeting was to provide an opportunity for scientists in the field of metal carcinogenesis and toxicology to discuss and compare their results. Sponsors for the conference were the National Institute of Environmental Health Sciences, the Nickel Producers Environmental Research Association and the International Lead and Zinc Research Organization.

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